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AUSTRALIA

Patents Act 1990

NOTICE OF ENTITLEMENT
(To be filed before acceptance)

We, **ELF ATOCHEM S.A.**, of Département Propriété Industrielle, 4 & 8 Cours Michelet, La Défense 10, 92800 Puteaux, France, being the applicant in respect of Application No. 12462/95 state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventors. The actual inventors are employees of the nominated person and under French law the nominated person is entitled to the grant of the patent.

The person nominated for the grant of the patent is the applicant of the application listed in the declaration under Article 8 of the PCT.

The basic application listed in the declaration made under Article 8 of the PCT is the first application made in a Convention country in respect of the invention.

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An advantage, among others, of the interfacial adhesion is associated with the better properties of the pipes (flexibility, a decrease in the crunching of the pipes and resistance to shocks) and a greater ease of use during the fixing of connections rather than using a pipe consisting of two separate parts (a rubber jacket and a thermoplastic liner).

Claim

1. A multilayer article consisting of a layer of elastomer moulded from a casting on a thermoplastic selected from PBT, mixtures containing polyvinylidene fluoride, and ethylene/vinyl alcohol and ethylene/tetrafluoroethylene copolymers, the elastomer adhering in itself to the thermoplastic.

4. A process for the preparation of a multilayer article according to claim 1, characterised in that the thermoplastic is moulded from a casting, by extrusion at an appropriate temperature, with the elastomeric layer consisting of a synthetic or natural elastomer containing carboxylic, epoxy or amino functional groups, an epichlorhydrin elastomer or mixtures of elastomers and a cross-linking

system, and characterised in that the layer of elastomeric composition is vulcanized.

7. A composite tubular article made up of an outer sheath of a vulcanized elastomer directly associated with a thermoplastic chosen from polyamide, PBT, mixtures containing polyvinylidene fluoride and ethylene/vinyl alcohol and ethylene/tetrafluoroethylene polymers.

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(54) Titre: ARTICLE MULTICOUCHE COMPRENANT UN ELASTOMERE VULCANISE ASSOCIE DIRECTEMENT A UN THER-
MOPLASTIQUE

(57) Abstract

A multilayer article including a functionalised, vulcanised elastomer self-adhered to a thermoplastic selected from polyamides, poly-
butyleneterephthalate, polyvinylidene fluoride containing mixtures and ethylene/vinyl alcohol and ethylene/tetrafluoroethylene copolymers.
A composite tubular article consisting of an outer sheet of vulcanised elastomer adhered to a hydrocarbon barrier thermoplastic or combined
with an inner sealing layer is also disclosed.

(57) Abrégé

Article multicouche comprenant un élastomère fonctionnalisé et vulcanisé adhérent en lui-même sur un thermoplastique choisi
parmi les polyamides, le PBT, les mélanges contenant le polyfluorure de vinylidène, les copolymères éthylène/alcool vinylique et
éthylène/tétrafluoréthylène. Article tubulaire composite formé d'une gaine externe d'élastomère vulcanisé adhérent sur un thermoplastique
barrière aux hydrocarbures ou associé à une couche interne d'imperméabilisation.

TEXT FOR FOREIGN FILINGS

MULTILAYER ARTICLE CONSISTING OF A VULCANIZED ELASTOMER
ASSOCIATED DIRECTLY WITH A THERMOPLASTIC

Description

The invention at hand relates to a multilayer article consisting of a layer of elastomer which is moulded on a thermoplastic from a casting and vulcanized so as to adhere directly to the latter.

The invention also relates to a process for the preparation of a composite article consisting of a vulcanized elastomer which is associated directly with a thermoplastic.

In the case where the thermoplastic has barrier properties against fuels or heat generating fluids, a double layer may be sufficient when the invention is applied to pipes for petrol or in air conditioning applications. To achieve the same purpose, in the case where the thermoplastic does not have barrier properties per se, one or (several) layer(s) will be needed in order to ensure permeability.

The processes which are commonly employed for assembling articles (tubular or sheet) made of vulcanized elastomer (synthetic or natural) that are associated with thermoplastics are based on the extrusion-sheathing of a thermoplastic previously coated with an adhesive. In the rubber industry the outer layer of elastomer is then usually vulcanized in an autoclave using hot air, steam or radiation.

However, in relation to the process a significant saving may be achieved by eliminating the application of the adhesive.

One of the purposes of the present invention is to propose a process for the preparation of a composite article as defined above, in which the application of adhesive is eliminated.

Another purpose of the invention is to propose an article such as the one defined above where the vulcanised elastomer sheath shows a high peel strength when subjected to a force of separation, preferably higher than 2 daN/cm.

The invention is intended to solve the following problems:

- the interfacial adhesion in the case of multilayer articles (particularly, in the case of tubular articles, between the outer elastomeric layer and the inner thermoplastic layer).
 - the protection of thermoplastic pipes against hot spots by a vulcanized elastomer, this is an example of an application in the motor vehicle industry.
- 5 - in the case of air conditioning ducting, the ducts are traditionally made of textile-reinforced rubber. Under new legislation, a barrier layer against fluorocarbons must be incorporated, and this is achieved with a barrier thermoplastic. This barrier thermoplastic layer must be thin so as not to impair the noise attenuation properties of the rubber.
- 10 - in the case of the application to petrol pipes, these pipes are made today of textile-reinforced rubber. The problems associated with the rubber are: permeability, swelling, a limited resistance to peroxidized fuel, and the extraction of various products, hence the advantage of introducing a thermoplastic inner barrier layer.

15 An advantage, among others, of the interfacial adhesion is associated with the better properties of the pipes (flexibility, a decrease in the crunching of the pipes and resistance to shocks) and a greater ease of use during the fixing of connections rather than using a pipe consisting of two separate parts (a rubber jacket and a thermoplastic liner).

20 Other advantages associated with the use of the present invention will be apparent in the following description.

Japanese Patent Application JP 5-44874 describes pipes with an outer layer of epichlorhydrin rubber and an inner layer of nylon or fluoro-resin, but includes the use of adhesive.

25 Patent Applications DE 4232946 and GB 2023626 also use an adhesion promoter or an adhesive for pipes made of polyamide (or fluoropolymer, in the former), covered with rubber.

30 French Patent FR 2660404 describes pipes produced by direct coextrusion of a vulcanizable elastomer on a polyolefine: the vulcanizable elastomer is selected from nitrile-PVC or EPDM rubbers and nothing is said regarding the vulcanization or the mechanism which makes the adhesion possible.

35 German Application DE 3914011 describes a pipe which consists of an outer layer of polyolefin elastomer (devoid of carboxylic or other functional groups) and a thermoplastic inner layer, for example polyamide, but in the application it is accepted that the use of

adhesive between the two layers would be preferable - furthermore this is explicitly described in a subsequent application DE 4026161.

A specialist will be familiar with the vulcanized synthetic or natural elastomers which are suitable for making use of the present invention: in the definition of the present invention the term "elastomer" means that it may consist of mixtures of several elastomers.

These elastomers or elastomer mixtures ^{preferably} exhibit a permanent compressive set (P.C.S.) at 100°C which is lower than 50%, generally between 5 and 40% and ^{more} preferably lower than 30%. These vulcanized elastomers originate from the corresponding vulcanizable elastomers.

Among the latter, mention can be made of natural rubber, polyisoprene which has a high double-bond content in a cis form, a polymerized emulsion based on a styrene/butadiene copolymer, a polymerized solution based on a styrene/butadiene copolymer, a polybutadiene which has a high double-bond content in a cis form, obtained by catalysis with nickel, cobalt, titanium or neodymium, a halogenated ethylene/propylene/diene terpolymer, a halogenated butyl rubber, a styrene/butadiene block copolymer, a styrene/isoprene block copolymer, the halogenated products of the above polymers, an acrylonitrile/butadiene copolymer, an acrylic elastomer, a fluoroelastomer, an epichlorhydrin elastomer and chloroprene.

Some of the elastomers mentioned above can be functionally grouped into carboxylic (or anhydride), epoxy or amino groups, by grafting these elastomers, using a known method, or, in the case of elastomer mixtures, grouped, for example, with acrylic elastomers.

Among the elastomers mentioned above, those which may be selected advantageously are included in the following group: carboxylate nitrile elastomers, acrylic elastomers, carboxylate polybutadienes, grafted ethylene/propylene/diene terpolymers, epichlorhydrin elastomers or mixtures of these polymers with the same elastomers but ungrafted, such as nitrile rubbers, hydrogenated nitriles, polybutadienes and ethylene/propylene/diene terpolymers, by themselves or mixed.

The thermoplastic may be selected from polyamides 6, 66, 11 and 12, preferably polyamides 11 and 12 (plasticized or otherwise) or their copolymers or compounds of these polyamides with polyolefines, or among polyesters (for example polybutylene terephthalate),

ethylene/tetrafluoroethylene (ETFE) copolymers, copolymers containing ethylene/vinyl

alcohol units and polyvinylidene fluoride (PVDF) or mixtures containing the latter.

Included in the term "polyvinylidene fluoride" is the homopolymer or the copolymers containing at least 70% by weight of vinylidene fluoride. The polyvinylidene fluoride may also be mixed with another thermoplastic polymer on condition that 50% by weight of polyvinylidene fluoride at least is present in the mixture.

5

An important example of a mixture containing polyvinylidene fluoride is the composition described in European Application EP 450994: a polymethacrylate plus an additive consisting of PVDF and of an acrylic or methacrylic elastomer.

- 10 The application of the invention therefore includes a layer of rubber adherent to a thermoplastic, but it may also consist of one or a number of other layers, possibly secured by a binder; therefore, one has: vulcanized rubber/thermoplastic/other layers with or without a binder, for example:

PA12/binder/PA6/EVOH/PA6 or PA12/binder/PVDF/PA12/PBT/PA12.

15

The invention is particularly useful for the sheathing of pipes which have one of the above mentioned thermoplastics as an outer layer: polyamides and their compounds, polyesters, etc.

- 20 Another application of the invention is a process for the preparation of the composite articles described above, characterized in that a thermoplastic is moulded from a casting, at an appropriate temperature, with an elastomeric composition consisting of a synthetic or natural elastomer possibly containing carboxylic (or dicarboxylic acid anhydride), epoxy or amino functional groups, a cross-linking system and possibly various adjuvants and fillers, and
25 characterised in that the layer of elastomeric composition obtained is vulcanized.

The vulcanization temperature is preferably between -50°C and $+30^{\circ}\text{C}$ of the Vicat point of the said thermoplastic in contact with the elastomer.

- 30 The elastomeric composition and its vulcanization kinetics are such that the duration of the vulcanization cycle does not exceed 15 minutes and that the vulcanized elastomer layer of the composite article exhibits a high peel strength (preferably higher than 2 daN/cm).

- Bearing in mind the intended use of the material, the vulcanized elastomers and
35 thermoplastics forming the composite material are normally joined with sufficient strength to prevent any separation during normal stress. Thus, within the meaning of the present text, the term "separation" implies the application to the material of a force which is considerably higher than that to which the said material would normally be subjected.

Separation resistance is assessed by a peeling test on a strip of pipe which is less than 5 mm in width, and cut along a generatrix. It is preferable and it will be an advantage if the peel strength is higher than 2 daN/cm.

- 5 In the case of a carboxylate unsaturated elastomer, the vulcanization of the rubber takes place thanks to the double bonds and the carboxylic groups; therefore it is necessary to prevent all of the latter, which are more reactive, from being consumed in the cross-linking, since they are needed for the adhesion with the thermoplastic. Therefore, the vulcanization temperature must be well controlled in order to have a sufficiently long scorch time and hence the
10 carboxylic groups which are still free are given time to react with the thermoplastic.

- According to an alternative process the thermoplastic layer is moulded from a casting by the elastomer composition which is extruded on an elastomeric extruder at a temperature of between 50°C and 120°C, in a sheathing die (that is to say a crosshead die). The
15 unvulcanized article is placed, possibly after cutting, in a conventional rubber vulcanization autoclave (particularly one using hot air, steam, infrared etc.) the temperature of which is between -5°C and +30°C of the Vicat point of the said thermoplastic in contact with the elastomer.

- 20 According to another alternative process the article is obtained by simultaneous coextrusion of the elastomer with the thermoplastic(s). In this case the adhesion produced during the coextrusion process and vulcanization operation is carried out consequentially or by reprocessing.

- 25 The vulcanization systems employed for producing these composites are well known to specialists and, consequently, the invention is not limited to process systems of any particular type. It is sufficient for the latter to meet the criterion relating to the vulcanization kinetics, as defined in the definition of the invention which is mentioned above.

- 30 When the elastomer has an unsaturated monomer base (butadiene, isoprene, vinylidenenorbornene, etc), mention may be made of four types of vulcanization systems:

- sulphur systems consisting of sulphur associated with usual accelerators such as dithiocarbamate metal salts (zinc or tellurium dimethyl-dithiocarbamate etc.), thiuram
35 disulphides (thiuram tetramethyldisulphide, etc.), sulpheramides, etc.

These systems may also contain zinc oxide used in combination with stearic acid.

- Sulphur-donor systems, in which most of the sulphur employed for bridging originates from sulphur-containing molecules such as the organosulphur compounds mentioned above.

- Systems containing phenolic resins, consisting of difunctional phenol-formaldehyde resins, which may be halogenated, used in combination with accelerators such as stannous chloride or zinc oxide.

5 - Peroxide systems. These make it possible to have a product which is white, more stable to heat, as in the case of sulphur-donor systems. Any free radical donors may be used (dicumyl peroxides etc.) in association with zinc oxide and stearic acid.

10 Where the elastomer is an acrylic (polybutyl acrylate with acidic or epoxy functional groups or any other reactive functional group permitting cross-linking), the usual cross-linking agents are used, which are based on diamines (ortho-tholuidylguanidine, diphenylguanidine etc.) or blocked diamines (hexamethylenediamine carbamate etc.).

15 Where the elastomer is an epichlorhydrin elastomer (homopolymer, copolymer or terpolymer), cross-linking agents based on amine (2-mercaptoimidazoline, triazines, etc.) are used.

20 The elastomeric compositions may be modified for some special properties (for example improvement in mechanical properties) by the addition of fillers such as carbon black, silica, kaolin, clay, talc, chalk etc. These fillers may be surface-treated with silanes, polyethylene glycols or any other coupling molecule. In general the proportion of fillers in parts by weight is between 5 and 100 per 100 parts of elastomers.

25 Moreover, the compositions may be made more flexible by using plasticizers such as petroleum-derived mineral oils, esters or phthalic acid or sebacic acid, liquid polymer plasticizers such as polybutadiene of low mass, possibly carboxylate, and other plasticizers which are well known to specialists.

30 The combinations of vulcanising agents which are used in the process should be such that they allow for the complete cross-linking of the elastomer according to kinetics which results in good resistance to separation, as mentioned in the definition of the invention and, in general, in good rubber properties (measured as a permanent compressive set at 100°C, tensile mechanical properties etc.).

35 The vulcanization temperature in the autoclave will be advantageously between 130 and 190°C.

Advantageously, the kinetics measured with the aid of an oscillating rheometer will be such that the characteristic time for a 90% vulcanization, t_{90} , does not exceed 15 minutes at 160°C and advantageously will be between 5 and 10 minutes.

Furthermore, it has been found that an important factor for obtaining materials which displays a good performance is a corresponding increase in torque of 0.2 Nm at the time when vulcanization begins (or setting time). Thus, it is advantageous that the above mentioned increase in torque should be reached in a time longer than or equal to 4 minutes at the moulding temperature, and preferably between 4 and 6 minutes.

EXAMPLES

The permeability of the pipes to petrol was measured by a static method at 23°C with fuel C containing 15% of methanol (static method).

Example 1, comparative

A composition produced in an internal mixer including, in parts by weight:

Chemigum NX 775 carboxylate nitrile elastomer (RCG 7343

elastomer, Goodyear trade name) 70

SK 70 PVC 30

15 Epoxidized soya oil 1.5

17 MOK tin octyl 0.3

Zinc stearate 0.3

DOP (dioctyl phthalate) 25

Wingstay 29 (antioxidant, 4,4-bis-2,2-dimethylbenzyl-diphenylamine

20 from Goodyear 1

Polyvest C 70 (carboxylate polybutadiene from HÜLS) 4

VN 3 silica (DEGUSSA FRANCE) 20

KS 300 silica (AKZO) 10

PEG 4000 (polyethylene glycol from HÜLS) 3

25 A 1100 silane (UNION CARBIDE) 1

TiO₂ 10

This composition was mixed on a roll with a vulcanization system of the following composition:

Sulphur 1

30 Vulkacit J (N,N'-dimethyl-N,N'-diphenylthiuram disulphide from BAYER) 2

MBS ((2-morpholino thio)benzothiazole) 2

Vulkalent E (sulphonamide from BAYER) 1

Stearic acid 1

35 ZnO 5

It was extruded on an elastomer extruder as a 6/10 mm pipe and then vulcanized at 160°C for 10 minutes.

The petrol permeability of this tubular article was 850 g/m² x 24 hours; the tubular article was found to be unmarked when folded and returned to its initial shape.

Example 2, comparative

- 5 An extruded pipe of PA 12 Rilsan AESNTL was produced in 6/8 mm diameter. The petrol permeability of this pipe was 80 g/m² x 24 hours per 1 mm thickness. When this tubular article is folded below a certain radius of curvature a crunching phenomenon occurs and the pipe is marked.

10 Example 3

- The pipe from Example 2 was taken up on an elastomer sheathing plant extruding the composition of Example 1 at 90°C through a sheathing die. The tubular article was then cut, slipped on 6 mm metal rods and placed in an oven at 170°C for 20 minutes. Its transverse dimensions after sheathing were 6/10 mm. The petrol permeability of this pipe is 80 g/m² x 24 hours (static value). This tubular article can be folded to a much smaller radius of curvature than the pipe of Example 2 and does not retain any fold mark.

Example 4, comparative

- 20 An extended pipe of PA 11 Rilsan BESNTL was produced in 6/8 mm diameter. The permeability of this pipe is 40 g/m² x 24 hours. When this pipe is bent below a certain radius of curvature, a crunching phenomenon occurs and the pipe is marked.

Example 5

- 25 The pipe of Example 4 was taken up on an elastomer sheathing plant extruding the composition of Example 1 at 90°C through a sheathing die. The tubular article was then cut, slipped on 6 mm metal rods, and placed in an oven at 180°C for 20 minutes. Its transverse dimensions after sheathing were 6/10 mm. The petrol permeability of this pipe is 40 g/m² x 24 hours. This tubular article can be bent to a much smaller radius of curvature than the pipe of Example 4 and does not retain any fold mark.

30 Example 6

A composition produced in an internal mixer including, in parts by weight:

Hydrin 2000 (copolymer of epichlorhydrin with ethylene oxide, R.M., from ZEON CHEMICALS)	100
Stearic acid	1
35 FEF N550 carbon black	30
Extrasil (silica from DEGUSSA FRANCE)	20
MgO	3
CaCO ₃	5

This composition was mixed on a roll with 1 part of ZISNET F (triazine from ZEON CHEMICALS).

- Furthermore a coextruded pipe of PA 12 Rilsan AESNTL and an Adhéflon[®] (of composition: 90% TPU/10% PVDF, hereafter referred to as DHP1) was produced in 6/8 mm diameter, with a 0.2 mm layer of DHP1. The petrol permeability of this tubular article is 80 g/m² x 24 hours. When this pipe is folded below a certain radius of curvature a crunching phenomenon occurs and the pipe is marked.
- 10 The above pipe was taken up on an elastomer sheathing plant extruding the Hydrin-based composition as specified above at 90°C through a sheathing die. The tubular article was then cut, slipped on 6 mm metal rods and placed in an oven at 170°C for 20 minutes. Its transverse dimensions after sheathing were 6/10 mm. The petrol permeability of this pipe is 80 g/m² x 24 hours. This tubular article can be folded to a much smaller radius of curvature
- 15 than the double-layer Rilsan 12/DHP1 pipe and does not retain any fold mark.

Example 7

- A coextruded pipe of PA 11 Rilsan BESNTL and an Adhéflon[®] (of composition: 35% of modified PMMA sold by ROHM and HAAS under reference Paraloid EXL 4151/30% of PVDF/35% of core/shell type acrylic elastomer with butadiene styrene core, sold by ROHM and HAAS under reference EXL 3361), hereafter referred to as DHP2, was produced in 6/8 mm diameter, with a 0.2 mm outer layer of DHP2. The petrol permeability of this tubular article was 40 g/m² x 24 hours. When this pipe is folded below a certain radius of curvature a crunching phenomenon occurs and the pipe is marked.

- 25 The above pipe was taken up on an elastomer sheathing plant, extruding the Hydrin-based composition specified in Example 6 at 90°C through a sheathing die. The tubular article was then cut, slipped on 6 mm metal rods and placed in an oven at 170°C for 20 minutes. Its transverse dimensions after sheathing were 6/10 mm. The petrol permeability of this pipe was 40 g/m² x 24 hours. This tubular article can be folded to a much smaller radius of curvature than the twin-layer Rilsan 11/DHP2 pipe and does not retain any fold mark.
- 30

Example 8:

- A coextruded pipe of PVDF and an Adhéflon[®] (DHP2) was produced in 6/7 mm diameter with a 0.2 mm external layer of DHP2. The petrol permeability of this tubular article is 10 g/m² x 24 hours.
- 35

The above pipe was taken up on an elastomer sheathing plant extruding the Hydrin-based composition specified in Example 6 at 90°C through a sheathing die. The tubular article was then cut, slipped on 6 mm metal rods and placed in an oven at 170°C for 20 minutes. Its transverse dimensions after sheathing were 6/8 mm. The petrol permeability of this pipe was 10 g/m² x 24 hours.

Example 9

A coextruded pipe of PA 11 Rilsan BESNTL and an Adhéflon® (DHP1) was produced in 6/8 mm diameter, with a 0.2 mm outer layer of DHP1. The petrol permeability of this tubular article was 40 g/m² x 24 hours. When this pipe is folded below a certain radius of curvature a crunching phenomenon occurs and the pipe is marked.

The above pipe was taken up on an elastomer sheathing plant extruding the composition based on XNBR carboxylate nitrile rubber specified in Example 1 at 90°C through a sheathing die. The tubular article was then cut, slipped on 6 mm metal rods and placed in an oven at 160°C for 20 minutes. Its transverse dimensions after sheathing were 6/10 mm. The petrol permeability of this pipe was 40 g/m² x 24 hours. This tubular article can be folded to a much smaller radius of curvature than the twin-layer Rilsan 11/DHP1 pipe and does not retain any fold mark.

Example 10

A coextruded multilayer pipe of PVDF 1000 HD, Adhéflon® (DHP2), PA 12 Rilsan AESNTL and another layer of Adhéflon® (DHP2) was produced in 6/8 mm diameter with a 0.15 mm PVDF inner layer, a 0.15 mm DHP2 intermediate layer and a 0.15 mm DHP2 outer layer. The petrol permeability of this tubular article is 10 g/m² x 24 hours.

The above pipe was taken up on an elastomer sheathing plant extruding the Hydrin-based composition specified in Example 6 at 90°C through a sheathing die. The tubular article was then cut, slipped on 6 mm metal rods and placed in an oven at 160°C for 20 minutes. Its transverse dimensions after sheathing were 6/10 mm. The petrol permeability of this pipe was 10 g/m² x 24 hours.

With regard to the before-mentioned examples it should be noted that:

Rilsan AESNTL is a trade mark of Elf Atochem and that PA 12 which is used in conjunction with the trade mark means Polyamide 12.

Rilsan BESNTL is a trade mark of Elf Atochem and that PA 11 5 which is used in conjunction with the trade mark means Polyamide 11.

Polyamide-12 is the polymer obtained by polycondensation of $\text{NH}_2\text{-(CH}_2\text{)}_{11}\text{-COOH}$, which contains 12 carbon atoms in the chain. Polyamide 11 is similar except it contains 11 carbon atoms instead of 12.

Adhéflon is a trade mark of Elf Atochem. The composition is: 90% 10 TPU/10% PVDF. It is also referred to as DHP1.

TPU means thermoplastic polyurethane.

PVDF means polyvinylidene fluoride $\text{-(CH}_2\text{-CF}_2\text{)}_n$

Modified PMMA is imidized PMMA by NH_3 or an amine.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A multilayer article consisting of a layer of elastomer^{which is} moulded from a casting on a thermoplastic selected from PBT, mixtures containing polyvinylidene fluoride, and ethylene/vinyl alcohol and ethylene/tetrafluoroethylene copolymers, the elastomer adhering in itself to the thermoplastic.
2. A multilayer article according to claim 1, characterised in that the elastomer is an epichlorhydrin elastomer or is functionally grouped with carboxylic, epoxy or amino groups.
3. A multilayer article according to claims 1 or 2, characterised in that the mixture containing polyvinylidene fluoride also includes polymethacrylate and elastomer.
4. A process for the preparation of a multilayer article according to claim 1, characterised in that the thermoplastic is moulded from a casting, by extrusion at an appropriate temperature, with the elastomeric layer consisting of a synthetic or natural elastomer containing carboxylic, epoxy or amino functional groups, an epichlorhydrin elastomer or mixtures of elastomers and a cross-linking system, and characterised in that the layer of elastomeric composition is vulcanized.
5. A process for the preparation of a multilayer article according to claim 1, characterised in that the thermoplastic is coextruded with the elastomer containing a cross-linking system and in that the layer of elastomeric composition is vulcanized.
6. A process according to claims 4 or 5, characterized in that the vulcanization may take place during the duplicate moulding or afterwards.

7. A composite tubular article made up of an outer sheath of a vulcanized elastomer directly associated with a thermoplastic chosen from polyamide, PBT, mixtures containing polyvinylidene fluoride and ethylene/vinyl alcohol and ethylene/tetrafluoroethylene polymers.

8. An article according to claim 7, wherein the tubular article is a pipe characterized in that the inner surface of the thermoplastic pipe may be coated with an impervious or protective inner layer which has barrier properties especially against liquids such as fuels or heat generating fluids.

DATED this 14th day of April, 1997

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ABSTRACT OF THE TECHNICAL CONTENT OF THE INVENTION**MULTILAYER ARTICLE CONSISTING OF A VULCANIZED ELASTOMER
ASSOCIATED DIRECTLY WITH A THERMOPLASTIC**

A multilayer article consisting of a functionally grouped and vulcanized elastomer, the elastomer adhering in itself to a thermoplastic selected from polyamides, PBT, and mixtures containing polyvinylidene fluoride, and ethylene/vinyl alcohol and ethylene/tetrafluoroethylene copolymers.

A composite tubular article made up of an outer sheath of vulcanized elastomer adherent to a thermoplastic acting as a barrier against hydrocarbons or associated with an inner layer to produce imperviousness.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/FR 94/01454

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B32B27/00 C08J5/12 F16L11/04 //B29K19:00,B29L23:00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J F16L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 344 427 (HULS) 6 December 1989 see page 2, line 16 - page 4, line 23 ---	1,2,4-8
X	DE,A,34 39 312 (TOYODA GOSEI) 15 May 1985 see page 12, line 5 - page 13, line 6 ---	1,2,4,5, 7
A	US,A,4 121 963 (YARDLEY ET AL.) 24 October 1978 see column 1, line 20 - line 23 see column 1, line 64 - column 2, line 8 ---	2,4
A	EP,A,0 303 244 (NIPPON ZEON) 15 February 1989 see claims --- -/--	2,3

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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E document member of the same patent family

Date of the actual completion of the international search

14 March 1995

Date of mailing of the international search report

04.04.95

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Attalla, G

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/FR 94/01454

C4(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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